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13. ABSTRACT (Maximum 200 words)

Sol-gel ceramic synthesis has drawn much interest in recent years. [1-5] Organometallic molecules, usually metal alkoxides, are polymerized in an alcohol/water solution with dissolved acids or bases to form a ceramic or glass material with exquisite chemical and microstructural control. Since the chemistry and microstructure of the solid determine its properties, this technology can be used to design materials with specified mechanical, optical, electronic, and physicochemical properties. These materials may be monoliths, films, fibers, or powders. Sol-gel synthesis offers a degree of control of composition and structure at the molecular level unachievable with traditional sintering or precipitation methods. It also offers an economical alternative to layered vapor deposition manufacture of coatings and fibers. Owing to their controlled chemistry and microstructure, sol-gel ceramics can be densified at much lower temperatures than conventional sintering temperatures, thereby saving energy and protecting delicate structures in the material itself or in its substrates. The microstructure can also be controlled to produce optical films, catalyst supports, monolithic ceramic bodies, etc. Since the precursor molecules are pure and dissolved, atomic placement and bonding can be controlled to tune mechanical, optical...

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Recent Progress in the Study of the Kinetics of Sol-Gel SiO$_2$ Synthesis Reactions

by

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Paper for the "International Symposium on Advances in Sol-Gel Processing and Applications"

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Recent Progress in the Study of the Kinetics of Sol-Gel SiO$_2$ Synthesis Reactions

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Overview of sol-gel technology

Sol-gel ceramic synthesis has drawn much interest in recent years. [1-5] Organometallic molecules, usually metal alkoxides, are polymerized in an alcohol/water solution with dissolved acids or bases to form a ceramic or glass material with exquisite chemical and microstructural control. Since the chemistry and microstructure of the solid determine its properties, this technology can be used to design materials with specified mechanical, optical, electronic, and physicochemical properties. These materials may be monoliths, films, fibers, or powders. Sol-gel synthesis offers a degree of control of composition and structure at the molecular level unachievable with traditional sintering or precipitation methods. It also offers an economical alternative to layered vapor deposition manufacture of coatings and fibers. Owing to their controlled chemistry and microstructure, sol-gel ceramics can be densified at much lower temperatures than conventional sintering temperatures, thereby saving energy and protecting delicate structures in the material itself or in its substrates. The microstructure can also be controlled to produce optical films, catalyst supports, monolithic ceramic bodies, etc. Since the precursor molecules are pure and dissolved, atomic placement and bonding can be controlled to tune mechanical, optical, electronic, and chemical properties and the product is free from traditional impurities. Halide and organic radical dopants can be added to the synthesis solution to tailor optical and mechanical properties of many devices (e.g., lasers, contact lenses).

The sol-gel technique promises to provide an alternative to such techniques as chemical vapor deposition in the formation of films or particles. As an example, it has been pointed out that the cost of optical quality SiO_2 fiber can be significantly reduced [6]. As the chemistry and physics of sol-gel systems come to be quantified, it will be possible to design surface chemistry. On such a surfaces we can expect the attachment of functional organic groups, catalytically active metals, metallization (on chips), optoelectronic connections, passivation coatings, and biologically active groups for chromatographic separation of drugs or DNA fragments. The porosity, surface area, and surface composition can be tailored for catalysts and chromatographic gels. Properties can also be varied continuously with the depth from the surface to produce, for instance, graded refractive index films and optical filters for signal processing or to control the interfacial mechanics and adhesion in composite ceramics.

However, if this potential is to be fully realized, the art of synthesis must be transformed into reaction engineering. Previous studies have revealed some qualitative kinetic trends, but lack functional relationships between the reactant structure and its reactivity are

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still lacking. This process offers the following attractive advantages over what has become traditional fiber or particle manufacture by CVD: 1) a wide range of multicomponent glass compositions, 2) easily varied compositions, 3) comparably high purity, 4) room temperature gel formation, 5) low sintering temperature, and 6) less stringent fiber drawing requirements [7a] Reaction rates and concentrations of reactants, intermediates, product, solvents, and catalysts are each complicated functions of time. Engineering of the ultimate microstructure and composition requires a quantitative understanding of a number of interdependent phenomena. The lack of understanding results in general processing problems such as nonuniform coating thickness, cracking, shrinkage, pinholes and limitations in the success of producing composites and multicomponent glasses. [2]

One of the most exciting possibilities offered by solgel technology is that of directing the synthesis of oxides in metastable and novel states. Since this is largely a problem of kinetics, it seems most profitable to investigate the used of agents which can direct the course of reaction along a desired path. It has been shown that dissolved acids and bases act as catalysts, directing the gelation of SiO_2 along markedly different paths; quantitative relationships between the chemical parameters and the structure of intermediates and products remains lacking. Furthermore, few systematic studies have encompassed important issues like the role of the metal substituent, of the catalyst, of the degree of ionization, of alkoxide exchange, and of transport.

Role of chemical kinetics in the synthesis of SiO2

The system that has received the most attention is SiO_2 because of its vast array of applications, because it serves as a component in an even wider spectrum of materials, and because its reactions serve as models for more general metal alkoxide reactions. Furthermore, SiO_2 serves as a model for other sol-gel systems with the simplification that unwanted hydroxides do not precipitate. [8] The remainder of this proposal, though, will describe the most pressing kinetic questions both for the SiO_2 system and for multicomponent (more than one oxide) systems. We will use the SiO2 synthesis system as an example.

In a typical preparation of SiO2, an alkoxysilane, alcohol, water, and either acid or base are mixed at atmospheric pressure and at temperatures ranging from 10 C to 100 C. The alcohol ensures the miscibility of the alkoxysilane and reduces the rate of reaction by diluting the reacting alkoxysilane and water molecules. This solution may be allowed to form a gel over a period ranging from hours to days, or at some point the partially polymerized solution may be

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coated onto a substrate or drawn into a fiber. The attention here, though, will be focused on the initial reactions that occur in the first part of the reaction.

Two types of reactions are primarily responsible for the formation of the initial structures and the determination of the ultimate material properties. The hydrolysis of the alkoxysilane by water replaces alkoxyl with hydroxyl groups, thereby rendering the silane active for low temperature polymerization:

$$Si(OR)_4 \rightarrow HOSi(OR)_3.$$
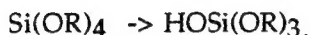
Condensation eliminates either water or alcohol to produce SiOSi linkages:

$$2\ HOSi(OR)_3 \rightarrow (RO)_3SiOSi(OR)_3 + H_2O$$
$$\text{or } (RO)_3SiOSi(OR)_2(OH) + ROH.$$
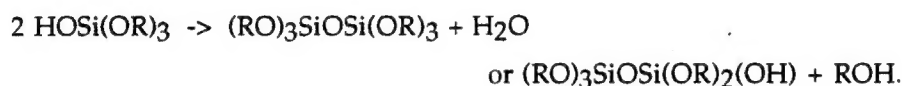
(where R is an alkyl group). Both hydrolysis and condensation appear to be catalyzed by the acid or base, but the effect and the mechanism of the catalyst action are not well understood quantitatively. Furthermore, each of these reactions may reach equilibrium over the course of the synthesis.

Though the reactions assumed above are written simply, it is important to recognize that over the course of the synthesis there can be <u>many</u> reactions of this type involving a myriad array of intermediate species of different sizes and composition. The rate coefficient of each reaction will vary with the catalyst and its concentration, the nature of the ligand on Si (OR, OH, or OSi), the number of each of these on a given Si, and temperature. Furthermore, there will be strong diffusional limitations to reaction as larger species are created. If each of these phenomena becomes better understood quantitatively it should be possible to regulate the synthesis selectivity and to control the ceramic structure in a fashion analogous to the accomplishments of polymer engineering.

There is already a great deal of empirical understanding of what means are available to control these reactions. The following selected observations are drawn from a number of studies which have used chromatography, small angle xray scattering, and NMR spectroscopy. [e.g., 9-12] These observations indicate how challenging it is to control all aspects of the polymerizing system using empirical observations alone and point out the need for a rigorous kinetic model.

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- Increasing the molar ratio of H_2O to alkoxysilane increases the molecular weight of intermediate polymers.

- Increasing the alkoxysilane concentration increases the molecular weight of the intermediate species and the average degree of polymer branching in the gel structure.

- Increasing the catalyst concentration increases the rate of gelation but decreases the intermediate polymer size.

- Increasing the size of the alcohol decreases the extent of reaction upon gelation.

- One of the most striking effects of the processing conditions on the product structure is seen with the choice of the polymerization catalyst. With the use of an acid catalyst, one gets a network of fibrous silica chains that interconnect into a relatively uniform gel, whereas with a base catalyst, one gets a particulate, almost colloidal gel. [12] The remainder of this proposal will focus on the effects of the catalyst on the course of polymerization.

It is important to use analytical methods which provide concentrations and structures of the many different reactive intermediate species in solution. For this reason there is increasing interest in employing spectroscopic and chromatographic tools to observe the evolution of intermediates during polymerization and gelation. One of the most promising techniques is nuclear magnetic resonance. NMR of ^{29}Si and ^{1}H have been used to follow the concentration of silicates with various degrees of hydrolysis and condensation in a few sol-gel systems. [13-17] This technique has the advantage of quantifying a large number of structures, including reasonably condensed ones (up to about 12 metal atoms). [18, 19] NMR also provides the opportunity to investigate the degrees of hydrolysis and condensation of new structures. Raman spectroscopy has also revealed some structural details of solutions and gels [20-22], and it has been used to quantify a small number of solution species, but most of the information available from Raman spectroscopy is also available using NMR spectroscopy.

NMR spectra have been used to roughly estimate some rate coefficients and to model a few isolated acid catalyzed systems. [23-24] Qualitative trends have been detected, but until recently little attention has been given to developing functional relationships between reaction rates and the chemistry of the precursors. Some experiments reported so far, though, are not necessarily quantitative, since it is not clear what the NMR relaxation rates or mechanisms are. Systematic NMR experiments with a range of catalytic conditions will provide a rational basis to develop a practical model and to extend the few observations to other systems and to engineer properties into materials.

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Effects of Composition on Reaction Rates and Selectivities - Expectations from Early Work

Reviewing the elementary reactions in SiO_2 synthesis, there are quantitative issues that remain unresolved. These issues also have impact on the synthesis of multicomponent gels. We may consider the contrast between the following qualitative predictions and the actual observations regarding the difference between acid-catalyzed and base-catalyzed sol-gel products. Here we review what has been qualitatively expected of the hydrolysis and condensation reactions. In the next section we review recent progress toward quantifying these trends.

Let us consider each elementary reaction type in turn. In order to later understand copolymerization selectivity, we must first review trends in the reactin rates for homopolymerization.

Nucleophilic hydrolysis of Si alkoxides

e.g., $Si(OR)_4 + OH^- + H_2O \rightarrow Si(OR)_4(OH)^- + H_2O \rightarrow Si(OR)_3(OH) + ROH + OH^-$

This is the presumed mechanism in base catalyzed systems. The hydroxide ion is thought to nucleophilically attack the positively charged Si atom. Since hydroxyls are less electron donating than alkoxyl groups, we expect the reactivity of the silicate tetrahedron toward nucleophilic hydrolysis to increase as hydroxyls replace alkoxyls. In other words, each subsequent hydrolysis should be easier.

The relative rate of subsequent hydrolysis steps have so far been rationalized by considering the electrostatic stabilization of the metal complex and by assuming that the rate limiting step is the nucleophilic attack. We are interested in these relative rates because 1) it will influence polymerization kinetics since as we increase the extent of the hydrolysis there are more functional groups available for condensation, and 2) an increase in the extent of hydrolysis can affect the molecular structure of the product, since a high degree of cross-linking and cyclization can occur. Keefer and others [Keefer 1984; Schaefer 1984; Brinker 1989] have reasoned that the OH is a less efficient charge donor than the OR group, so with each subsequent hydrolysis the partial charge on the metal should become even more positive, and consequently each subsequent hydrolysis step should have a larger rate constant. This trend has not been verified quantitatively, but only qualitatively [Pouxviel 1987; Turner1987]. In Si alkoxide systems in alkaline medium, hydrolysis is slow compared to condensation, and the competing

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effects must be modelled quantitatively to deduce hydrolysis rates. This trend has nevertheless been used as an explanation for the formation of highly crosslinked, colloidal SiO_2 particles in alkaline conditions [Keefer 1984], but this explanation remains incomplete since hydrolysis has rarely gone to completion before gelation [Pouxviel 1987; Assink 1988; Orcel 1986] and since the condensation reaction is reversible in alkaline conditions.

Electrophilic hydrolysis of Si alkoxides

e.g., $Si(OR)_4 + H^+ + H_2O \rightarrow Si(OR)_3(OHR)^+ + H_2O \rightarrow Si(OR)_3(OH) + ROH + H^+$

This is the presumed mechanism of hydrolysis in acid catalyzed systems. The hydronium ion is thought to electrophilically associate with the negative charge center near the silicate oxygen sites. We might expect the rate to change as the extent of hydrolysis increases in the following way. The alkoxyl groups are more electron donating than are hydroxyls, so the reactivity toward electrophilic hydrolysis should decrease as hydroxyls replace alkoxyls. In other words we might expect each subsequent hydrolysis to be more difficult. [11]

By this mechanism (wherein an electrophile such as the hydronium ion attacks one of the negatively charged alkoxide ligands), Keefer and others [Keefer 1984; Brinker 1990] have proposed that each subsequent hydrolysis proceeding should decrease in rate since the partial charge on the attacked (victim) alkoxide ligand becomes less negative. This argument again assumes that the rate is limited by the attacking step. Some NMR results [Turner 1987] have seemed to confirm this trend, but the study only involved one system with a very limited amount of hydrolysing water. Other NMR results [e.g., Pouxviel 1987] have found that in excess water, each subsequent hydrolysis step seems to proceed more quickly!

The relevant literature offers little consistency in the kinetic data of the acid catalyzed hydrolysis of TEOS [McGrath 1987; Kelts 1985; Orcel 1986; Dent Glasser 1980; Che 1988]. Recently we have used Si-29 NMR in conjunction with numerical simulations to measure hydrolysis rate constants under conditions where we could decouple the effect of hydrolysis and condensation reactions [Sanchez 1991]. For the monomers, each subsequent hydrolysis becomes kinetically more favored, thus confirming some earlier studies. However, we also found that each subsequent hydrolysis produces a thermodynamically less stable hydrolyzed monomer. Kinetic and thermodynamic stability trends thus oppose each other, explaining the presence of a distribution of hydrolyzed monomers rather than a complete and immediate hydrolysis.

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Comparison of "expected" hydrolysis trends

Neither of the trends in hydrolysis rates has been carefully verified until recently, though the electrophilic trend has been supported qualitatively. [17, 24] Thus, in predicting the product structure, one is limited to educated guesses subject to serious error.

In the past, these two trends were taken to explain the difference observed between the acid-catalyzed and base-catalyzed sol-gel product. [11] X-ray scattering results show that the acid-catalyzed gel is fibrous with few interconnections whereas the base-catalyzed gel consists of highly interconnected rings and cages, so on a microscopic scale it appears particulate, almost colloidal. Upon drying monolithic glass bodies made with basic catalysts resist cracking better and have larger pores.

The formation of the structure was understood in the following way. During synthesis in acid conditions only a few hydrolyzed groups were thought to exist on any Si, so polymerization proceeded in one direction with little branching. In basic conditions, the reasoning went, perhaps many hydrolyzed groups could be formed at one Si site, so polymerization would proceed with many branching points.

It has recently become apparent, though, that this explanation is insufficient. With the first rough hydrolysis rate measurements, it became clear that electrophilic hydrolysis is so fast that many hydrolyzed groups exist on each Si early in the synthesis - sometimes even before any measurable condensation has occurred! [14, 24, 25] Though the absolute rate of nucleophilic hydrolysis remains controversial [e.g., 16, 25-27], nucleophilic hydrolysis is understood to proceed much more slowly than electrophilic hydrolysis. The nucleophilic hydrolysis step is in fact so slow that it may remain incomplete even after full gelation has occurred [16, 26]! It is clear we need to learn both the absolute rate of hydrolysis for individual species (various OR, OH, and OSi substituents) and precisely how these rates change with reaction conditions if we are to understand these confusing structural results and to predict structures from new multicomponent processes.

It remains unclear why acid-catalyzed gels are fibrous if electrophilic hydrolysis proceeds quickly and thus presumably provides a large number of polymerization active sites. Two possible reasons concern the hydrolysis reactions. The first, suggested by Pouxviel et al [24], is that as the synthesis proceeds the ratio of k_h/k_c decreases, where k_h is the hydrolysis

rate constant and k_c is the condensation rate constant. This hypothesis has been supported qualitatively [24, 28] and is consistent with the prediction arising from the electrophilic substitution mechanism that, since an OSi group is less electron donating than an OH group, k_h should generally decrease as the synthesis proceeds.

The second possibility is that the electrophilic hydrolysis reaction is reversible and reaches equilibrium. [11, 29] In this case the approach to hydrolysis equilibrium may be fast, but the extent of hydrolysis remains incomplete, thereby preventing branched condensation. The reactivity of the precursors for hydrolysis and condensation is also affected by the number and nature of the alkoxide (OR) group, and these groups are subject to exchange during the synthesis. It is therefore necessary to quantify the role of alkoxide exchange:

$$SiOR + R'OH = SiOR' + ROH$$
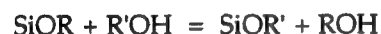
and reesterification (i.e., the reverse of hydrolysis):

$$SiOH + ROH = SiOR + H_2O$$

(only one Si substituent is shown). Though Keefer [11] hypothesized that this reaction does not take place in basic solution since the ionized silanol groups would repel attack by an alcohol, the electrophilic attack mechanism suggests the opposite. In fact, Pouxviel et al [24] have used ^{1}H NMR to prove that the ethoxide/propoxide exchange rate is pronounced in acidic solutions.

Nucleophilic condensation of Si alkoxide derivatives

e.g., $2 (XO)_3Si(OH) + OH^- \rightarrow (XO)_3SiO^- + (XO)_3SiOH + H_2O \rightarrow (XO)_3SiOSi(OX)_3$
$$+ H_2O + OH^-$$
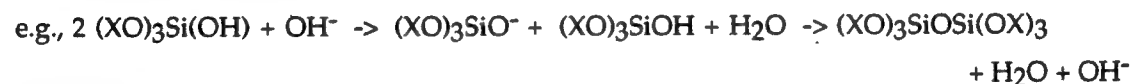
where X = R, Si, or H.

Polymerization is believed to proceed by nucleophilic condensation:

$2 (TO)_3Si(OH) + OH^- \rightarrow (TO)_3SiO^- + (TO)_3SiOH + H_2O \rightarrow (TO)_3SiOSi(OT)_3$
$$+ H_2O + OH^-$$
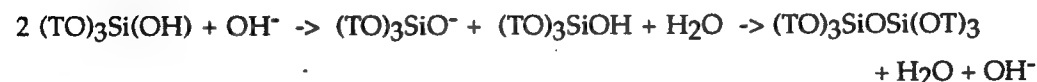
where T = R, Si, or H. The hydroxide ion charges one of the silicate groups and then the ionized silicate attacks the positive charge of another Si.

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Until recently there has been little more than qualitative indication of how the condensation rate is affected by reactor composition and other processing parameters. This mechanism suggests that the rate should be proportional to the concentration of the hydroxide ion. Since nucleophilic condensation requires inversion of one of the reacting molecules, it is expected that the condensation rate should decrease both with alkoxide size and with the extent of silicate condensation.

Examining the condensation rate as a function of the catalyst will allow one to test the remaining three hypotheses proposed in the literature regarding the contrast between acid and base catalyzed gels. First, Brinker et al [29] and Keefer [11] suggest that the fastest condensation rate will be between the most acidic and the most basic groups, and since these are the most highly condensed and least condensed silicates. A large, highly condensed intermediate will tend to annex a small intermediate, and this fosters the agglomeration of colloid-like species. This idea is supported experimentally by size exclusion chromatography results indicating a bimodal size distribution of the intermediates in these systems. [30] Another reason for this rate trend would be that the large oligomers could not invert in the way that is required by nucleophilic attack, so large oligomers could only react with monomers and not with other oligomers [31].

Secondly, base-catalyzed systems may produce colloid-like particles because poorly condensed silicate groups are highly soluble in basic solution. [32-34] In other words, the condensation reaction is reversible for poorly condensed silicates at high pH. This moves the system towards an equilibrium where all silicate tetrahedra are highly condensed, since fibrous structures just dissolve. This process, termed Ostwald ripening, may only occur in basic solutions, since prepolymerized precursor structures do not decompose in acid conditions, whereas in basic conditions linear polymers first dissolve to monomers. [19] Furthermore, Brinker et al found that even fibrous silicates reformed to more compact structures upon exposure to base catalyst. [22, 29] Thus one should investigate the reversibility of various condensation reactions as the pH changes. Selective NMR excitation [18, 35] can be used to trace the transfer of material between species with various degrees of condensation and to measure rates of reaction.

Finally, the more condensed base-catalyzed products may be attributed to cyclization reactions that take place only with base catalysis or with a high catalyst concentration. None of the early works considered this, though the formation of the three-membered ring by

condensation of silicic acid was carefully established using Si NMR by Engelhardt et al [36]. One should perform careful experiments in these conditions to detect whether small rings are formed.

Two classes of reactions are thought to compete in the polymerization step: condensation with the elimination of alcohols or condensation with the elimination of water. Using partial charge calculations on the transition state, previous workers [Livage 1988] have predicted that alcohol producing condensation is kinetically preferred, but this disagrees with some NMR measurements [Pouxviel 1987, Kay 1988]. However, these experiments were performed on Si alkoxide systems in acid conditions, where hydrolysis is quite fast and reversible; neither this nor solvent effects were accounted for in the modelling.

The relative rate of condensation for (groups with different numbers of MOM linkages) has been qualitatively deduced by several authors, who argue that since the OM ligand is a poorer charge donor than either OH or OR, the metal center should become more susceptible to attack as it becomes more condensed. On the other hand, the attacking nucleophilic group will be more negatively charged when it belongs to a completely uncondensed monomer. Therefore the fastest condensation reaction should be between a monomer and a highly condensed group (often denoted Q^0 and Q^3, respectively, for Si) [Keefer 1984; Aylett 1979]. This idea is supported experimentally by size exclusion chromatography results indicating a bimodal size distribution of the intermediates in these systems [Yoldas 1986]. Another reason for this rate trend would be that the large oligomers could not invert in the way that is required by nucleophilic attack, so large oligomers could only react with monomers and not with other oligomers [Brinker 1988].

Thus we see that it is inappropriate to assign a condensation rate constant to only one of the reactants; instead, a condensation rate constant will be characteristic of the particular *pair* of reactants. Even if we were to ignore variation with different degrees of hydrolysis (a rash assumption), the number of distinct condensation rate constants that must be found may be enormous. This is an excellent argument to develop meaningful quantitative *relationships* to reduce the number of arbitrary constants that must be measured.

Nucleophilic condensation can well be reversible, leading to Ostwald ripening. Base-catalyzed SiO_2 systems may produce colloid-like particles because poorly condensed silicate groups are highly soluble in basic solution [Iler 1980; Klein 1984; Zerda 1986]. In other words, the condensation reaction is reversible for poorly condensed silicates at high pH. This moves the system towards an equilibrium where all silicate tetrahedra are highly condensed, since fibrous

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structures just dissolve [Engelhardt 1987]. This process may occur for any situation where the oxolation reaction approaches equilibrium. Furthermore, Brinker et al found that even fibrous silicates reformed to more compact structures upon exposure to base catalyst. [Brinker 1986; Aylett 1979]

Recent progress

Nucleophilic hydrolysis: role of ionic equilibria

In order to form intermediates selectively, it is important to know precisely how rate coefficients change with the concentration and type of catalyst. A recurrent problem in comparing the rates and the role of the catalyst is the difficulty in quantifying the concentration of the hydroxide or hydronium ion. Consider here two examples wherein careful attention must be paid to the ion concentration. First, if the nucleophilic hydrolysis mechanism is written correctly, we expect that the hydrolysis rate should increase linearly with the base concentration. This is generally true except at high pH, where the rate increases less than linearly with the base concentration because hydroxide ions are consumed in the ionization of silicates [32]:

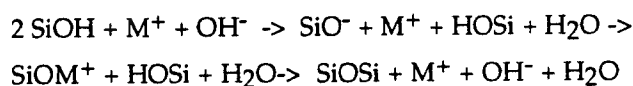$$(TO)_3SiOH + OH^- \rightarrow (TO)_3SiO^- + HOH \quad (T = R, O, \text{ or } Si)$$
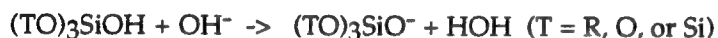
In another example, Schmidt et al [37] found that with increasing water concentration the hydrolysis rate decreased in an HCl catalyzed system whereas it increased in NH_4OH. The only explanation for this is that in the first case the addition of water diluted the active catalyst (H^+) whereas in the second it allowed more base dissociation. Qualitative trends alone cannot predict such results.

To develop a quantitative understanding of both acid and base catalysis, one should monitor the degree of ionization of the reactants by carefully measuring the ^{29}Si and ^1H NMR chemical shifts to detect changes in the average degree of ionization of silicates and water, respectively. Harris et al [38] have shown this effect using the Si chemical shift, and H NMR can reveal hydronium and hydroxide ion concentrations owing to the influence of these species on the chemical shift of H_2O due to rapid chemical exchange. Harris has also shown that methanol changes the point of zero charge of silicate anions from pH=2 to pH=4 [39]; thus one should measure the ionization of precursors in the mixed solvents used in sol-gel synthesis. This can be done by measuring the hydroxide or hydronium ion concentration with a glass electrode,

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taking changes in solvent permittivity into account by monitoring water and alcohol concentrations with NMR over the course of the synthesis. It is expected that the solvent will seriously affect ionic equilibria [32] and thus direct the polymerization chemistry [40] by shielding charged groups and ions either through permittivity effects or by furnishing a solvation shield.

It has been found that an even higher degree of control over the synthesis selectivity is available by selecting which acid or which base catalyst to use. [24, 41, 42] For instance, Kelts et al [25] noticed that the choice of the base catalyst affected the monomer consumption and the rate of gelation. Thus the counterions may fill an additional structure directing role. It is known that cations can catalyze the dissolution of silica [32], and NMR has revealed ion pairing by alkali metals in hydroxide solutions and in zeolite synthesis solutions. [18] One can perform cation NMR chemical shift measurements with variously sized precursors to investigate the hypothesis that ion pairs are reactive intermediates as in the following reaction :

$$2 \, SiOH + M^+ + OH^- \rightarrow \, SiO^- + M^+ + HOSi + H_2O \rightarrow$$
$$SiOM^+ + HOSi + H_2O \rightarrow \, SiOSi + M^+ + OH^- + H_2O$$

(only one Si substituent is shown). Cation selective electrode measurements will be used to corroborate these measurements.

Since its cation is volatile, NH_4OH is the most widely used base catalyst in sol-gel synthesis and it deserves special attention. It has been shown that NH_4^+ and other quaternary ammonium cations can direct the structure of silicates in alkaline alcohol/aqueous solutions, shifting the silicate equilibrium shifts to cage-like anions, so one can investigate the effect of these structure directors on intermediates in sol-gel synthesis. [19] It is also known that at high temperature the ammonium cations equilibrate with amine and alcohol [43], e.g.,

$$ROH + NH_4^+ = NH_3R^+ + HOH$$
$$NR_4^+ + OH^- = NR_3 + ROH.$$
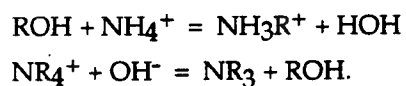
One can use ^{13}C NMR to quantify the effect of this equilibrium on the availability of both ammonium and hydroxide ion.

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A number of authors have reported that the choice of acid catalyst also affects the gelation rate. [27, 41] One can use multinuclear NMR to detect whether the acid counterion interacts with the condensing silicates. For instance, the use of HF the flourine ion displaces the hydroxide or alkoxide from the silane to form SiF bonds.

We have recently examined the effects of various base catalysts on the reaction kinetics. Gel times were monitored for a variety of precursor solutions. Apparent activation energies are calculated using a simplified kinetic model incorporating well-justified mechanistic assumptions. The trends of gel times and activation energies were compared to rationalize the action of the catalyst.

Over the course of these reactions the solution increases in viscosity, finally setting into a solid gel at the gel time. Determining the gel time visually is often difficult since the gelation may not be a distinct, rapid process. This is particularly troublesome for base catalyzed systems. Some researchers have found it useful to monitor the viscosity, taking an arbitrary value to define the gel point. Alternatively, we can use a protocol by which one may observe a distinct gel point in base catalyzed systems; one must "prehydrolyze" the alkoxide using a very small concentration of acid before adding the base catalyst for condensation.

When adequate water is present, and if a prehydrolysis protocol is used, we can assume that hydrolysis is rapid and comes to equilibrium. With a molar composition of 1 TEOS: 4 EtOH: 4 H2O: 0.001 HCl: 0.001 MOH (where M=alkaline cation), the gel times increase in the order $Rb^+ < NH_4^+ < Na^+$. However, if the concentration of prehydrolyzing acid is decreased to 0.0005 HCl / 1 mol TEOS, the order is changed to Rb+ < Na+ < NH4+. In order to probe the molecular structure of the polymer with changing acid concentration, ^{29}Si NMR spectra were acquired. From these spectra it was evident that decreasing the HCl concentration strongly affects the structure of the polymers; the lower acid concentration results in an increase in the amount of singly hydrolyzed monomer and nonhydrolyzed endgroups, whereas it eliminates both doubly hydrolyzed middle groups and cyclic species.

For a given acid concentration (HCl / TEOS = 0.001) the apparent condensation rate coefficient increases at room temperature in the order $Na^+ < NH_4^+ < Rb^+$ (the reverse of the trend in gel time). Were the catalyst to act only to moderate the condensation activation energy, then the measured activation energy should decrease in the order $Na^+ > NH_4^+ > Rb^+$. However, the measured values in fact decrease in the order $NH_4^+ > Na^+ > Rb^+$. Similar

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discrepancies were noted for the reaction carried out with an acid content of 0.0005 HCl / 1 TEOS.

One explanation that has been proposed for unexpected trends in activation energy is the onset of diffusional limitations. However, diffusional limitations should cause a bending of the Arrhenius curve to give an anomalously low activation energy, since the diffusion of silicates in solution requires only about 4 kcal/mol. We observed no such manifestations.

We have also presented cation NMR evidence of ion-pair complexation in base-catalyzed sol-gel systems, comprised of TEOS, water and ethanol. The cation NMR lines allow us to deduce whether the cation is coordinated to ethanol, water or silicates. Furthermore, we have tested three theoretical models to predict the stability of the ion-pair which is detected by NMR. First, we consider a simple electrostatic model based on formal charges. Second, we use a model developed by Livage and Henry. These authors have pioneered the application of electronegativity equalization to predict sol-gel precursor reactivities through the use of a partial charge model based on Allred-Rochow electronegativities and Sanderson's principle of electronegativity equalization. However, this model might not successfully predict the current results. Finally, we consider a model proposed by Bergmann and Hinze, which is based on bond orbital electronegativity equalization (BOEE). We show that this model predicts complex stability in accord with experiment.

These studies suggest the following order of efficacy of the cation at competing for charged surface silicate sites:

$$Li^+ < Na^+ < Cs^+ = NH_4^+ < Rb^+ < K^+$$
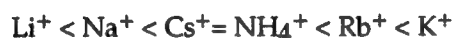
K^+ has been observed to produce the fastest condensation of monomeric silicic acid and produces the fastest base catalyzed TEOS gelations, yielding a spinnable gel. We propose that cation complexation may cause these results. In order to explain the relative equilibrium of cation-silicate pairs, we next pursue a theoretical investigation.

The ion-pair reaction can be written:

$$M^+ \cdots OH_2 + {}^-OSi = M^+ \cdots {}^-OSi + H_2O$$

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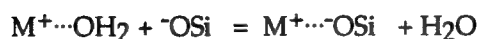
where M^+ is Li^+, Na^+, K^+, Rb^+ or Cs^+. The reaction represents the competition between a surface silicate group and a water of hydration for the position next to the cation. Note that we are ignoring other waters of hydration, assuming that they will not affect the reaction enthalpy change.

It appears that the ion-pair equilibrium results from the balance between solvation of the cation and strength of the ion-pair bond. For instance, though the $Li^+\cdots^-OSi$ bond is the strongest, Li^+ is so strongly solvated that the ion-pairing is less favorable compared with the other cations. Furthermore, the $K^+\cdots^-OSi$ bond is more favored than might have been expected since K^+ holds the hydrating water less tightly and at the same time the $K^+\cdots^-OSi$ bond is strong enough. Potassium represents thus the best compromise with its moderate size and its low enough electronegativity. The experimental trend, and in particular the high stability of the potassium ion-pair, is thus explained by our calculations, at least qualitatively.

Acid-catalyzed hydrolysis

The alcoholic solutions of tetraethoxysilane ($Si(OR)_4$, where $R = C_2H_5$) are among the most intensively studied sol/gel systems.[1] Generally both hydrolysis and condensation take place simultaneously, and thus the kinetic simulations and the interpretation of the results are often difficult. In acidic solutions, the condensation reactions are much slower than the hydrolysis and are thus rate-limiting for the kinetics of the reaction.[2,3] However, the hydrolysis is far from being a negligible part of the gelation process; for example, it appears that the degree of hydrolysis has very important consequences regarding the nature of the condensed intermediates and thus indirectly on the kinetics of gelation and the structure of the gel formed.

Though the relevant literature offers little consistency in the kinetic data of the acid catalyzed hydrolysis of silicon alkoxides, reliable rate constants are essential for the development of kinetic models for sol-gel processing. Si-29 NMR was used in conjunction with numerical simulations to measure hydrolysis rate constants for tetraethoxysilane (TEOS), tetramethoxysilane (TMOS) and hexaethoxydisiloxane. Unlike previous efforts, we have used conditions where the effects of hydrolysis and condensation reactions can be decoupled. We have verified our rate constants using a range of solution composition. Implications regarding the influence of the synthesis protocol on gel homogeneity are discussed. We have also evaluated the enthalpies, entropies and activation energies for the hydrolysis of TEOS and TMOS.

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We find that each subsequent hydrolysis reaction has a higher rate constant, confirming some earlier studies. However, we also find that each hydrolysis step becomes thermodynamically less favorable. These opposing kinetic and thermodynamic trends explain why acid catalyzed hydrolysis produces a distribution of hydrolyzed intermediates rather than just fully hydrolyzed products. They also suggest that complete and immediate hydrolysis would be difficult to achieve except at very high water concentration.

Condensation

Octaethoxytrisiloxane, $[EtO]_3Si-O-Si[OEt]_2-O-Si[OEt]_3$, was synthesized and then polymerized in water/alcohol solution in presence of an acid catalyst. The concentrations of intermediates formed during the reaction were monitored by ^{29}Si-NMR. The rate constants for the polymerization reactions were estimated by computer simulations and the rates of linear and cyclic condensation were compared. Surprisingly, the formation of cyclic species by ring closure was much faster than previously assumed. This suggests that kinetic models for the silicon alkoxide sol-gel processes need to account for cyclization at very early stages of the polymerization.

Despite the success of equal reactivity random branching (Flory-Stockmayer) theory in predicting features of the batch gelation of organic condensation polymers, improved models are required for inorganic condensation polymerization. We examine the kinetic trends of hydrolysis and condensation reactions of silicon alkoxides in both acid and alkaline solution. Oligomeric intermediates of various molecular weights are prepared; ^{29}Si NMR, chromatography, and kinetic simulations are used to determine rate constants for the many various hydrolysis and condensation reactions. Quantitative trends among these constants are used to determine characteristic reactivities of various sites in response to both inductive and steric influences. These reactivities depend strongly on the environment of the reacting site. Implications for the development of the gel structures are explored using cascade theory with first shell substitution effects.

Though nonideal kinetics and molecular size distributions early in reaction can be attributed to the first shell substitution effect, we also show that this alone is not sufficient to explain reaction near gelation. For example, cyclization due to intra-molecular condensation causes the critical gel conversion to increase dramatically. Partly owing to cyclization, reactive groups become inaccessible to each other. Thereafter, kinetics are governed by reacting site mobility. We study the selectivity for cyclization and the mobility of the silicate polymers using a

variety of NMR techniques. The onset of cyclization and mobility controlled kinetics is incorporated into the model using branching tree theory with conversion dependent probability generation functions.

Thus, while it is widely acknowledged that the condensation rate coefficient should decrease dramatically as the polymer grows, we have been able to quantify the actual substitution effect of the substitutions OR ->OH and OH->OSi for a number of oligomers. These studies show several remarkable trends. For hydrolysis, all steps are reversible and are slowed mainly by the operation OR->OSi. For condensation, the rate coefficient, as Keefer (11) suggested, depends on the chemistry of BOTH of the reacting pairs, but in odd ways. For instance, in the substituion OR->OH, the rate constant increases but is sensitive only to one of the reacting pair. In the substitution OH->OSi, the rate constant decreases and is sensitive to the environment of both members of the reacting pair.

Role of Molecular Transport

In many polymerization problems it is important to understand the role of reactant diffusion. Though experimental and theoretical evidence may indicate that a particular molecule would be highly reactive toward hydrolysis or condensation, the product may possess structural features that betray this expectation if the reaction involving the precursor structure is limited by its transport to other reactive sites. Atkins [48] points out that for a simple bimolecular reaction between A and B, the measurement of the apparent rate constant may actually only be a measure of the diffusivity of the molecules:

$$k_2 = 4 \, p \, R \, (D_A + D_B) \, N_a,$$

where k_2 is the rate coefficient, R is the collision radius, D_A and D_B are the diffusivities of molecules A and B, and N_a is Avogadro's number.

As the condensation of alkoxysilanes proceeds, the viscosity of the system increases markedly. Since the viscosity is related in the first approximation to the diffusivity by the Stokes-Einstein relation:

$$D = kT/6 \, p \, h \, a,$$

(where D is the diffusivity, k is Boltzmann's constant, T is temperature, h is the viscosity, and a is the molecular radius) it is clear that the most crucial structure-directing reactions become diffusion-limited during the course of the synthesis. Pouxviel [24] has reported that the measured condensation rate decreases as the degree of condensation increases, but it is not clear whether one can conclude that the reactivity of the polymer decreases with increasing condensation, since this trend may only reflect the inhibited mobility of the more condensed species. Also, increasing the catalyst concentration can decrease the molecular weight of intermediates [10], which may suggest that, though the intermediates react as fast as possible, they may only occasionally encounter other intermediates. Diffusion limitations may also help explain why the base catalyzed system gels much more quickly than the acid catalyzed system, since in the former small species diffuse to a large species whereas in the latter two large ones must diffuse together.

One can also perform pulsed-field gradient experiments using the H signal of various metal alkoxides to estimate their diffusivity. [19] Finally, one can corroborate these results with predictions of diffusivity from viscosity measurements. In this way one can develop a more accurate model of the synthesis and also be able to distinguish between the observed rates of reaction and the intrinsic reactivity of silicate structure. Our long-range plans are to complement these experimental studies with molecular dynamics modelling studies to predict the effect of diffusion on the ultimate product structure.

^{29}Si NMR and gas chromatography were recently used to investigate the degree of polymerization while varying the extent of reaction for acid catalyzed TEOS hydrolysis and condensation. Comparison with the Carothers equation indicated that the limited degree of polymerization observed was mainly the consequence of a low average monomer functionality. The low functionality is due to an excess of silicon-bonded ethoxy groups and the presence of monofunctional silanols. Our results indicate that the reactive monomers in acid-catalyzed, low water concentration systems are of mixed functionalities, and that the molecular growth occurs randomly only for a limited range of early conversion. The observed gelation for systems with water-to-silicon ratio of 2 or greater may be explained by the cancellation of stoichiometric imbalance between the hydroxyl and ethoxy functional groups.

Several authors have suggested that diffusion limitations may play a role in the development of the microstructure of sol-gel ceramics, but recent studies have shown that the sizes of the intermediates should be so small that it is difficult to understand how diffusion limitations can come to play a role. To investigate whether diffusion coefficients are readily predicted, we

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have examined silicates in the acid catalyzed hydrolysis and condensation of tetraethyl orthosilicate in a solution with the molar composition TEOS : EtOH : H_2O : HCl = 1 : 4 : 0.8 : 0.0008 using ^1H pulsed-gradient-spin-echo NMR, ordinary ^{29}Si and ^1H NMR, as well as gas chromatography. A low water concentration is used in order to preserve the proton signal from the silicon-bonded ethoxy group which is needed for diffusion measurements and to reproduce conditions that should lead to weakly branched, homogeneous gels. The average mobility of the silicate species drops initially from 0.90 x 10^{-5} cm^2/s to 0.56 x 10^{-5} cm^2/s, but as condensation proceeds, the average mobility stays constant for 250 hours, and then increases slightly. Our results show that the mobility of the silicon precursors is reduced both with increasing molecular weight and with the extent of hydrolysis. Complexation with the water molecules reduces the diffusivities of the hydrolyzed species by increasing the effective hydrodynamic radii. We attribute the late rise in mobility to the loss of hydrogen bonding as the silicon hydroxyl groups and water are consumed. Although the early stages of reactions are clearly not diffusion-limited, and the polymerization process occurs randomly [ ] with no mobility influence, our results suggest that hydrogen bonding may be important in slowing the motion of intermediates in the presence of high water concentration.

Summary

Sol/gel chemistry has emerged as a singularly powerful method to synthesize high-tech oxide catalysts, ceramics, glasses, and gels, but this synthesis remains an art. It has long been argued that by controlling the rate of hydrolysis and condensation of precursor alkoxides one can control the ultimate composition and structure of the solid. In the near future three key issues should be resolved:

1) how can the hydrolysis catalyst direct the structure of the oxide?,

2) what is the rate of sequential hydrolysis reactions, and how does that explain the range of polymerizing precursors present?,

3) how do diffusion and the number of hydrolyzed sites govern the size distribution of intermediates?

Using NMR spectroscopy, we have shown the following points regarding the processing of silica gels, and we have developed predictive models that will serve the community of researchers synthesizing these materials:

1) Base catalysts can be used to influence the structure largely because the base complexes directly with the intermediate oligomers.

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2) Acid catalysts provide a range of hydrolyzed intermediates NOT because sequential hydrolysis reactions grow slower (as was previously thought), but because of a competition between increasingly favorable kinetics on the one hand and increasingly unfavorable thermodynamics on the other.

3) Cyclization reactions are extremely fast and must be incorporated into gelation models.

4) While diffusion does not influence the rate of early oligomerization reactions, it is extremely sensitive to the polarity of the oligomer and of the medium; this phenomenon may become important at later stages of reaction (near gelation to the solid).

5) The size of the growing intermediates is well predicted by Flory-Stockmayer theory only for a short time provided that one can accurately characterize the degree of hydrolysis. After this time, reaction rate models will have to become more detailed.

Acknowledgements

References

1. Uhlmann, D.R., in Better Ceramics Through Chemistry, MRS Symp. Proc Vol. 32, Elsevier, 1984, p.59.

2. Uhlmann, D.R. and G.P. Rajendran, in Ultrastructure Processing of Advanced Ceramics (J. D. Mackenzie and D. R. Ulrich, eds.), Wiley, New York, 1987, p.241.

3. Zelinski, B.J.J., and D. R. Uhlmann, J. Phys. Chem. Solids, 45(10) 1069, 1984.

4. Sowman, H. G., Ceramic Bulletin, 67 (12), 1911, 1988.

5. Klein, L.C., Ann. Rev. Mat. Sci., 15, 227, 1985.

6. Schmidt, H. et al, J. Non-Cryst. Sol., 83 1, 1984.

7. Brinker, C.J. et al , J. Non-Cryst. Sol., 48, 47, 1988.

7a. Geisler, J.A. et al., "Optical Fibres", European Patent Office, The Hague, The Netherlands, 1986.

8. Partlow, D. P., proceedings of "Chemical Processing of Interfaces and Microstructures," sponsored by the Am. Chem. Soc., in Minneapolis, MN 1988.

9. Balfe, C.A. and S.L. Martinez, <u>Better Ceramics Through Chemistry II</u>, MRS Symp. Proc. Vol. 73, Mat. Res. Soc, 1986, p. 27.

10. Yoldas, B.E. , <u>J. Non-Cryst. Sol.</u> <u>82</u> 11, 1986.

11. Keefer, K. D. in <u>Better Ceramics Through Chemistry</u>, MRS Symp. Proc Vol. 32, Elsevier, 1984, p. 15.

12. Schaefer, D.W., and K. D. Keefer, in <u>Better Ceramics Through Chemistry</u>, MRS Symp. Proc Vol. 32, Elsevier, 1984, p.1.

13. Jonas, J. et al., in <u>Ultrastructure Processing of Advanced Ceramics</u> (J. D. Mackenzie and D. R. Ulrich, eds.), Wiley, New York, 1987, , p. 303.

14. Assink, R. A. and B. D. Kay, <u>J. Non-Cryst. Sol.</u>, <u>99</u>, 359, 1988.

15. Pouxviel, J. C. et al, <u>J. Non-Cryst. Sol.</u>, <u>89</u>, 345, 1987.

16. McGrath, J.E. et al, in <u>Ultrastructure Processing of Advanced Ceramics</u> (J. D. Mackenzie and D. R. Ulrich, eds.), Wiley, New York, 1987, p.55.

17. Turner, C.W. and K. J. Franklin, <u>J. Non-Cryst. Sol.</u> <u>91</u> 402, 1987.

18. McCormick, A. et al, in press, <u>J. Phys Chem.</u>

19. Engelhardt, G., and D. Michel, "High Resolution Solid State NMR of Silicates and Zeolites," Wiley, New York, 1987.

20. Mulder, C.A.M. and A. A. J. M. Damen, <u>J. Non-Cryst. Sol.</u>, <u>98</u>, 169, 1987.

21. Lippert, J.L., et al., <u>J. Non-Cryst. Sol.</u>, <u>104</u>, 139, 1988.

22. Brinker, C.J. et al., <u>ACS Polym. Prep.</u> <u>28</u>(1) 428, 1986.

23. Kay, B.D., and R. A. Assink, <u>J. Non-Cryst. Sol.</u>, <u>104</u>, 112, 1988.

24. Pouxviel, J. C. and J. P. Boilot, <u>J. Non-Cryst. Sol.</u>, <u>94</u>, 374, 1987.

25. Kelts, L. W. et al, <u>J. Non-Cryst. Sol.</u>, <u>353</u>, 1985.

26. Dent Glasser, L.S. and D. N. Smith, <u>JCS Chem. Comm. 727</u>, 1980.

27. Che, T. M. , J. J. Rafalko, and P. B. Dorain, in <u>Ultrastructure Processing of Advanced Ceramics</u> (J. D. Mackenzie and D. R. Ulrich, eds.), Wiley, New York, 1987, p.827.

28. Klemperer, W., et al., in <u>Better Ceramics Through Chemistry II</u>, MRS Symp. Proc. Vol. 73, Mat. Res. Soc, 1986, p. 15.

29. Aylett, B. J., "Organometallic Compounds," Chapman and Hall, London, 1979.

29. Brinker, C. J. et al, <u>J. Non-Cryst. Sol.</u>, <u>63</u>, 45, 1984.

30. Yoldas, B.E. , <u>J. Non-Cryst. Sol.</u>, <u>83</u> 376, 1986.

31. Bailey, J.K., and M. L. Mecartney, in <u>Proceedings of the 46th Annual Meeting of the Electron Microscopy Society of America</u> (G. W. Bailey, ed.), San Francisco Press, San Francisco, 1988.

32. Iler, R. K., "The Chemistry of Silica," Wiley, New York, 1980.

33. Klein, L.C. and G. J. Garvey, in <u>Better Ceramics Through Chemistry</u>, MRS Symp. Proc Vol. 32, Elsevier, 1984, p.33.

34. Zerda, T.W. et al, J. Non-Cryst. Sol., 81 365, 1986.

35. Creswell, C. J., et al., J. Chem. Soc., Chem. Comm., 1261, 1984.

36. Engelhardt, G. et al, Zeit. fur Anorg. und Allg. Chem., 428, 43, 1977.

37. Schmidt, H. , in Better Ceramics Through Chemistry, MRS Symp. Proc Vol. 32, Elsevier, 1984, p.327.

38. Harris, R. K., and C.T.G. Knight, J. Chem. Soc., Faraday 2, 79, 1525, 1983.

39. Harris, R.K. , and C.T.G. Knight, JCS Chem. Comm., 726, 1980.

40. Artaki, I., et al, J. Non-Cryst. Sol., 81, 381, 1986.

41. Colby, M. W. et al, J. Non-Cryst. Sol., 82, 37, 1988.

42. Sakka, S. et al, in Ultrastructure Processing of Advanced Ceramics (J. D. Mackenzie and D. R. Ulrich, eds.), Wiley, New York, 1987, , p.159.

43. Barrer, R. M., "Hydrothermal Chemistry of Zeolites," Butterworths, London, 1982.

44. Basil, J.D. and C.-C. Lin, in Ultrastructure Processing of Advanced Ceramics (J. D. Mackenzie and D. R. Ulrich, eds.), Wiley, New York, 1987, , p.783.

45. Irwin, A.D., et al., J. Non-Cryst. Sol., 101, 249, 1988.

46. Pouxviel, J.C. and J.P. Boilot, in Ultrastructure Processing of Advanced Ceramics (J. D. Mackenzie and D. R. Ulrich, eds.), Wiley, New York, 1987, , p.197.

47. Livage, J. and M. Henry, in Ultrastructure Processing of Advanced Ceramics (J. D. Mackenzie and D. R. Ulrich, eds.), Wiley, New York, 1987, , p.183.

48. Atkins, P.W., Physical Chemistry, Oxford Press, Oxford, 1978.

49. Miller, D.R., and C.W. Macosko, Macromolecules, 9, 206, 1976.

50. Knight, C. T. G. , J. Non-Cryst. Sol., 104, 151, 1988.

51. Kosinski, S.G., J. Non-Cryst. Sol., 105, 45, 1988.

52. Mainz, V. et al., Better Ceramics Through Chemistry III, Mat. Res. Soc, 1988.

53. Dent Glasser, L.S., and G. Harvey, J. Chem. Soc., Chem. Comm., 1250, 1984.

54. Derouane, E.G., et al., Zeolites, 2, 299, 1982.

55. Deverell, C., in "Progress in NMR Spectroscopy" (J.W. Emsley et al., eds.) vol. 4, Pergamon, Oxford, 1969, p.235.

56. Fukushima, E. and Roeder, S., "Nuclear Magnetic Resonance: A Nuts and Bolts Approach," Addison-Wesley, Reading, MA, 1981.

57. Ray, N. H., and Plaisted, R. J., J. Chem. Soc., Dalton Trans., 475, 1983.

58. Klemperer, W., and S.D. Ramamurthi, ACS Polymer Preprints 28(1), 432, 1987.

59. Wheeler, G. , in Ultrastructure Processing of Advanced Ceramics (J. D. Mackenzie and D. R. Ulrich, eds.), Wiley, New York, 1987, p.819.

60. Griscom, D. L., J. Non-Cryst. Sol., 24, 155, 1977.